Coexisting charge modulation and ferromagnetism produces long period phases in manganites: new example of electronic soft matter.

G.C. Milward, M.J. Calderón, P.B. Littlewood

Cavendish Laboratory, Cambridge University,

Madingley Road, Cambridge CB3 0HE, UK

(Dated: February 2, 2008)

The phenomenon of colossal magnetoresistance in manganites is generally agreed to be a result of competition between crystal phases with different electronic, magnetic, and structural order; a competition which can be strong enough to cause phase separation between metallic ferromagnet and insulating charge modulated states [1, 2, 3, 4, 5]. Nevertheless, closer inspection of phase diagrams in many manganites reveals complex phases where the two order parameters of magnetism and charge modulation unexpectedly coexist[6, 7]. Here we show that such experiments can be naturally explained within a phenomenological Ginzburg-Landau theory. In contrast to models where phase separation originates from disorder [8] or as a strain induced kinetic phenomenon [9], we argue that magnetic and charge modulation coexist in new thermodynamic phases. This leads to a rich diagram of equilibrium phases, qualitatively similar to those seen in experiment. The success of this model argues for a fundamental reinterpretation of the nature of charge modulation in these materials from a localised to a more extended "charge density wave" picture. The same symmetry considerations that favour textured coexistance of charge and magnetic order may apply to many electronic systems with competing phases. The resulting "Electronically soft" phases of matter with incommensurate, inhomogeneous and mixed order may be general phenomena in correlated systems.

The manganese perovskites ($RE^{3+}_{1-x}AE^{2+}_{x}MnO_3$, RE rare earth, AE alkaline earth) provide a laboratory to study the interplay of a variety of magnetic, electronic and structural phases of matter in a strongly correlated electronic system. As in many strongly correlated electronic systems, the basic paradigm for manganite physics is the competition between the delocalising effects of the electron kinetic energy and the localising effects of the Coulomb repulsion, aided by coupling to lattice degrees of freedom. When the kinetic energy is dominant, one finds a metallic ground state with ferromagnetic alignment of the core moments. When the localising effects preponderate, instead we see charge and/or orbitally ordered ground states with substantial local lattice distortions from the near cubic symmetry of the metal, along with insulating behaviour and antiferromagnetism. One may tune between these two phases by many external parameters, especially chemical substitution, but also lattice strain, and magnetic field. The competition between metal and insulator is famously evident in the phenomenon of bulk colossal magnetoresistance, where a magnetic field tunes the conductivity of the material, and even more clearly in the strong tendency toward phase separation and inhomogeneity and regimes of percolative transport.

The origin of charge and orbital ordered phases is still the subject of debate. Charge modulation has been traditionally seen as the ordering of Mn^{4+} and Mn^{3+} ions[10]. More recently, the charge disproportionation of the Mn ions has been argued to be much smaller than one[11, 12, 13] but still the idea of two kinds of cation forming stripes prevails and is used to interpret the experiments. In such a scenario, one expects a density x of one kind of cation and $1-x$ of the other. The charge modulation would be given by the averaged wave-vector $\mathbf{q} \approx (1-x)\mathbf{a}^*$ with $\mathbf{a}^*$ the reciprocal lattice vector, aside from possible commensuration effects near special dopings ($x = 1/2, 2/3, 3/4$).

However, this picture is not compatible with the experimental findings on commensurate and incommensurate modulation, summarised in Fig.1. At half-doping, commensurate modulation is expected and found at low temperatures, together with antiferromagnetism of the CE type [10]. Above the Néel temperature, though, the modulation is incommensurate [7, 14, 15]. When found to be charge modulated, underdoped samples ($x < 0.5$) do not show the relation $\mathbf{q} \approx (1-x)\mathbf{a}^*$, rather the modulation wave-vector is always commensurate with $\mathbf{q} = 0.5\,\mathbf{a}^*$ [16, 17, 18, 19] and independent of temperature. Finally, the overdoped samples ($x > 0.5$) show the expected incommensurate wave-vector [19] below the Néel temperature, decreasing above it [20]. However, no sign of discommensurations, but a uniform

incommensurate modulation, has been found in recent experiments on $La_{1-x}Ca_xMnO_3$ [21].

Another experimental conundrum is the coexistence of charge modulation and ferromagnetism despite their natural antipathy. For instance, at half-doping, the incommensurate modulation above the Néel temperature is accompanied by ferromagnetism [7]. A different electronic phase showing ferromagnetism and charge modulation has also been found at low temperature in $La_{0.5}Ca_{0.5}MnO_3$ [6]. Slightly overdoped samples can also be ferromagnetic above Néel temperature [22, 23]. Another example of coexistence is given by the underdoped ($0.3 < x < 0.5$) $Pr_{1-x}Ca_xMnO_3$. The ground state is commensurate and charge-modulated [16, 17] but the antiferromagnetism is canted [18, 24, 25], showing a ferromagnetic component coexisting with the commensurate charge modulation.

One might propose to explain these phenomena in terms of microscopic theory incorporating the many different couplings and microscopic degrees of freedom, but this is a daunting task that might not be illuminating owing to its complexity. Here we propose a simple and more transparent phenomenological approach to this problem by means of Ginzburg-Landau theory. We will show how the close interplay of ferromagnetism and charge modulation conspires to reproduce the experimental findings just discussed.

Ginzburg-Landau theory allows the study of phase transitions in a phenomenological way and it consists in expressing the free energy as a power expansion of the order parameters and their gradients. The order parameters we consider here are the magnetisation $M(r)$ and the charge-orbital modulation $\psi(r) = \rho(r)e^{i(\mathbf{Q_c}.\mathbf{r}+\phi(r))}$. r is the spatial coordinate, ρ is the amplitude of the modulation, $\mathbf{Q_c} = \frac{\mathbf{a}^*}{n}$ is a wave-vector commensurate with the lattice and ϕ is the phase that would incorporate structures with incommensurate periodicities. To simplify the discussion we study a one dimensional scalar modulation, since charge modulation within a domain occurs only in one direction. $n = 4$ gives the correct periodicity for the lattice distortions measured in $x = 0.5$ as, though the charge modulation has period 2, the orbital order follows a zig-zag pattern with period 4. Notice that if $\nabla\phi = 0$, ψ is a wave of amplitude ρ and wave-vector commensurate with the lattice. If $\nabla\phi \neq 0$, the wave-vector is $\mathbf{Q_c} + \langle\nabla\phi\rangle$ and therefore, in general, cannot be expressed as a simple rational number of $\mathbf{a}^*$.

The free energy density can be separated into three contributions: magnetisation, charge

modulation and coupling terms. The first two are

$$\mathcal{F}_M = \frac{1}{2}a_M(T-T_c)M^2 + \frac{1}{4}b_M M^4 + \frac{1}{2}\xi_M^2(\nabla M)^2, \tag{1}$$

$$\mathcal{F}_\psi = \frac{1}{2}a_\rho(T-T_{CO})\rho^2 + \frac{1}{4}b_\rho\rho^4 + \frac{1}{2}\xi_\rho^2(\nabla\rho)^2 + \frac{1}{2}\xi_\rho^2\rho^2\left(\nabla\phi - q_o\right)^2 + \frac{1}{n}\eta\rho^n\cos(n\phi) \tag{2}$$

The magnetic energy, $\mathcal{F}_M$, taken alone will describe a phase transition to homogenous magnetism below the Curie temperature T_C. $\mathcal{F}_\psi$ is the free energy extensively used to study commensurate-incommensurate phase transitions of charge density waves, spin density waves or modulated lattice distortions [26]. $q_o = 1/2 - x$ is the predicted deviation (by chemical composition) from commensurability around $x = 0.5$. The term $\frac{1}{2}\xi_\rho^2\rho^2\left(\nabla\phi - q_o\right)^2$ favours a uniform incommensurate modulation with $\nabla\phi = q_o$. On the other hand $\frac{1}{n}\eta\rho^n\cos(n\phi)$ is an Umklapp term that favours commensurability with $\phi = 2\pi j/n$, j integer (for $\eta < 0$). Taken alone, this describes two phases. Upon cooling below T_{CO}, the amplitude ρ of the charge density wave rises from zero but provided $n > 2$, the Umklapp term is small and the modulation is incommensurate. As temperature is lowered, ρ grows, the Umklapp term may become dominant and a lock-in transition occurs if η is comparable to ξ_ρ^2.

We now discuss coupling between the two order parameters. The lowest order coupling term which arises is $d_1\rho^2M^2$ so that there is a free energy penalty for homogeneous coexistence of magnetism and charge modulation. Were this the only coupling term the free energy would be generally stabilised either by a homogenous magnetisation or by charge modulation, depending on which transition temperature is the larger. Next one can of course introduce uniform coupling terms of higher powers of M and ρ, but they make no qualitative changes unless they have a negative sign. More interesting is that there is a leading order coupling term in the *gradient* of the form $d_2\rho^2M^2(\nabla\phi - q_o)$. The fact there is a term *linear* in the gradient is expected because there is no symmetry about $x = 1/2$; different signs of the gradient correspond physically to compression or extension of the CDW period, i.e. to extra "3+" or "4+" sites. One can also justify this term microscopically: if we consider the effect of charge modulation on the Fermi surface, then it is clear that if we choose a wave vector which does not match the chemical doping, one will be left with small pockets of carriers at the Fermi surface; these metallic electrons (or holes) are then available to mediate double exchange and thereby promote ferromagnetism. The asymmetry around $x = 1/2$ is due to the asymmetry between electron and hole pockets. Now note that this gradient term can be incorporated into Eq. 2 by completing the square, and replacing q_o by

$$q_{eff} = q_o - \frac{d_2}{\xi_\rho^2} M^2 = \frac{1}{2} - x - \frac{d_2}{\xi_\rho^2} M^2 \quad . \tag{3}$$

The sign of d_2 is unknown *a priori* and we here choose it to be positive. Once this sign is fixed, however, this gradient coupling has profound consequences for the phase diagram. First, note that even if we are at commensurability ($x = 1/2$), if magnetism is present, then there is a tendency to *incommensurate* charge modulation. This reproduces the experiments of Chen et al. [7], on $La_{1/2}Ca_{1/2}MnO_3$, where the onset of charge modulation is incommensurate, and accompanied by ferromagnetism - which is replaced by Néel order at the transition to the commensurate phase. The incommensurate phase of $Pr_{1/2}Ca_{1/2}MnO_3$ (see Fig. 1) is paramagnetic [14] but accompanied by the onset of ferromagnetic spin fluctuations [15, 27]. The second feature of this term is that if $x < 1/2$, it is possible for coexisting magnetism to "cancel" the chemical tendency to incommensurability, and we note that canted magnetism is generally reported [18, 24, 25] in the underdoped manganites that show commensurate charge modulation. No such cancellation is possible for $x > 1/2$, and thus the dog-leg dependence of wave-vector on doping shown in the inset to Fig. 1 is indicated.

These features are reproduced by numerical minimisation of the coupled free energy with appropriate values of the parameters. Figure 2 shows the generic form of the phase diagram that can be obtained. In Fig. 3 we show an explicit evaluation of the temperature- and doping-dependence of the magnetism and (in)commensurability for parameters chosen to approximately reproduce the experimental regimes. The parameter range that can be used without altering the main features in Figs. 2, 3 is quite wide provided charge modulation dominates over magnetic order.

Throughout much of the phase diagram shown in these figures, the order parameters M, ρ and $\nabla\phi$ are approximately uniform in space, at least for the parameters we have chosen. However, close to the commensurate-incommensurate transition, the phase modulation becomes non uniform, and the phase gradient is built up by periodic discommensurations where the phase advances through $2\pi/n$. In such an inhomogeneous state, magnetism is naturally enhanced at the boundary and the amplitude of the charge modulation suppressed (see Fig. 4). Another situation where inhomogeneity is enforced is at a magnetic domain wall, where it can be energetically preferable to have a sharp wall stabilised by an insertion of local charge modulation. Such a phenomenon might be responsible for the anomalously

large resistance reported for magnetic domain walls in $LaCaMnO_3$ [28, 29].

When interpreting experimental results in the light of the theory presented here, a couple of issues must be kept in mind. Firstly, the theory proposed is a mean field theory that cannot describe strong fluctuations as its solutions are uniformly ordered or disordered phases. However, experimentally there are some regimes, like the incommensurate phase of $Pr_{1/2}Ca_{1/2}MnO_3$, where strong ferromagnetic fluctuations have been measured [15, 27], rather than the long range magnetic order we would predict. Secondly, in order to keep the calculations tractable, the phase transitions have been forced to be continuous. This explains why the reentrant magnetism above T_L shown in Fig. 2 appears only when $T_C > T_{CO}$. If this theory were generalised to include discontinuous phase transitions, this condition would relax. Another consequence of assuming continuous phase transitions is that phase separation cannot be predicted. In real systems phase separation is possible since strain [3, 9], or disorder [8], can make more or less localised phases dominate within a given region. Orbital ordering is described by a vector order parameter, thus our simple model cannot address the complexity of different orbitally ordered phases that have been proposed [12].

The Ginzburg-Landau phenomenology we propose is capable of systematizing some puzzling data for manganites near $x = 1/2$, but of course the propensity for mixed and homogeneous phases is driven by the underlying physical parameters that make the energetic cost of spatial fluctuations low. This "electronic softness" means that as well as spatially disordered "phase separation", one finds new ordered phases which are long period arrangements of the two competing orders. It may indeed be that this potential for textured electronic phases is a hallmark of electronic oxides near the Mott transition [30], seen perhaps in the co-existence of density waves and superconductivity in the cuprates [31].

Acknowledgements.

The authors thank L. Brey and N. Mathur for helpful discussions. PBL thanks the National High Magnetic Field Laboratory of the Los Alamos National Laboratory for hospitality. MJC acknowledges Churchill College, University of Cambridge, for the award of a JRF. This work was supported by the EPSRC and through the EPSRC Magnetic Oxide Network.

---

[1] M.B. Salamon and M. Jamie, The physics of manganites: structure and transport, *Reviews of Modern Physics* **76** 583 (2001)

[2] N.D. Mathur and P.B. Littlewood, Mesoscopic textures in manganites, *Physics Today* **56**, 25-30 (2003).

[3] N.D. Mathur and P.B. Littlewood, The self-organised phases of manganites, *Solid State Communications* **119**, 271-280 (2001).

[4] E. Dagotto, Nanoscale phase separation and colossal magnetoresistance, Springer Series in Solid State Sciences, Vol 136.

[5] M. Uehara, S. Mori, C.H. Chen and S.-W. Cheong, Percolative Phase Separation underlies colossal magnetoresistance in mixed-valence manganites, *Nature* **399**, 560-563 (1999).

[6] J.C. Loudon, N.D. Mathur and P.A. Midgley, Charge-ordered ferromagnetic phase in $La_{0.5}Ca_{0.5}MnO_3$, *Nature* **420**, 797-800 (2002).

[7] C.H. Chen and S.-W. Cheong, Commensurate to Incommensurate Charge Ordering and Its Real-Space Images in $La_{0.5}Ca_{0.5}MnO_3$, *Physical Review Letters* **76**, 4042 (1996).

[8] A. Moreo, M. Mayr, A. Feiguin, S. Yunoki, and E. Dagotto, Giant Cluster Coexistence in Doped Manganites and Other Compounds, *Physical Review Letters* **84**, 5568-5571 (2000).

[9] K.H. Ahn, T. Lookman and A.R. Bishop, Strain-induced metal-insulator phase coexistence in perovskite manganites, *Nature* **428**, 401-404 (2004).

[10] J. Goodenough, Theory of the Role of Covalence in the Perovskite-Type Manganites [La, M(II)]MnO3, *Physical Review* **100**, 564 (1955).

[11] J. García, M.C. Sánchez, J. Blasco, G. Subías and G. Proietti, Analysis of the x-ray resonant scattering at the Mn K edge in half-doped mixed valence manganites, *Journal of Physics: Condensed Matter* **13**, 3243-3256 (2001).

[12] L. Brey, Continuous Charge Modulated Diagonal Phase in Manganites, *Physical Review Letters* **92** 127202 (2004).

[13] Coey M, Charge ordering in oxides, *Nature* **430** 155-156 (2004).

[14] S. Mori, T. Katsufuji, N. Yamamoto, C.H. Chen and S.-W. Cheong, Microstructure related to charge and orbital ordering in $Pr_{0.5}Ca_{0.5}MnO3$, *Physical Review B* **59**, 13573 (1999).

[15] R. Kajimoto, H. Yoshizawa, Y. Tomioka and Y. Tokura, Commensurate-incommensurate transition in the melting process of orbital ordering in $Pr_{0.5}Ca_{0.5}MnO_3$: A neutron diffraction study, *Physical Review B* **63**, 212407 (2001).

[16] M.v. Zimmermann, C.S. Nelson, J.P. Hill, D. Gibbs, M. Blume, D. Casa, B. Keimer, Y. Murakami, C.-C. Kao, C. Venkataraman, T. Gog, Y. Tomioka, and Y. Tokura, X-ray resonant

scattering studies of orbital and charge ordering in $Pr_{1-x}Ca_xMnO_3$, *Physical Review B* **64**, 195133 (2001).

[17] S. Larochelle, A. Mehta, N. Kaneko, P.K. Mang, A.F. Panchula, L. Zhou, J. Arthur, and M. Greven, Nature of e_g electron order in $La_{1-x}Sr_{1+x}MnO_4$, *Physical Review Letters* **87**, 095502 (2001).

[18] Z. Jirak, S. Krupicka,Z. Simsa, M. Dlouha and S. Vratislav, Neutron diffraction study of $Pr_{1-x}Ca_xMnO_3$ perovskites, *Journal of Magnetism and Magnetic materials* **53**, 153-166 (1985).

[19] C.H. Chen, S.-W. Cheong, and H.Y. Hwang, Charge ordered stripes in $La_{1-x}Ca_xMnO_3$, *Journal of Applied Physics* **81**, 4326 (1997).

[20] C.H. Chen, S. Mori and S.-W. Cheong, Anomalous melting transition of the charge ordered state in manganites, *Physical Review Letters* **83**, 4792-4795 (1999).

[21] J.C. Loudon, S. Cox, A.J. Williams, J.P. Attfield, P.B. Littlewood, P.A. Midgley and N.D. Mathur, Uniform periodicity in stripe phase $La_{1-x}Ca_xMnO_3$ at arbitrary doping, cond-mat/0308581, submitted to *Physical Review Letters*.

[22] P. Schiffer, A.P. Ramiresz, W. Bao and S-W. Cheong, Low Temperature Magnetoresistance and the Magnetic Phase Diagram of $La_{1-x}Ca_xMnO_3$, *Physical Review Letters* **75**, 3336 (1995)

[23] R. Kajimoto, H. Yoshizawa, H. Kawano, H. Kuwahara, Y. Tokura, K. Ohoyama and M. Ohashi, Hole-concentration-induced transformation of the magnetic and orbital structures in $Nd_{1-x}Sr_xMnO_3$, *Physical Review B* **60**, 9506 (1999).

[24] Y. Tomioka, A. Asamitsu, H. Kuwahara, Y. Moritomo, and Y. Tokura, Magnetic-field-induced metal-insulator phenomena in $Pr_{1-x}Ca_xMnO_3$ with controlled charge-ordering, *Physical Review B* **53**, 1689 (1996).

[25] Yoshizawa H, Kawano H, Tomioka Y,Tokura Y, Neutron diffraction study of the magnetic-field-induced metal-insulator transition in $Pr_{0.7}Ca_{0.3}MnO_3$, *Physical Review B* **52**, R13145-R13148 (1995).

[26] J.C. Tolèdano and P. Tolèdano, The Landau Theory of phase transitions. World Scientific, 1987

[27] R. Kajimoto, T. Kakeshita, Y. Oohara, H. Yoshizawa, Y. Tomioka, and Y. Tokura, Anomalous ferromagnetic spin fluctuations in an antiferromagnetic insulator $Pr_{1-x}Ca_xMnO_3$, *Physical Review B* **58**, R11837 (1998).

[28] Mathur ND, Littlewood PB, Todd NK, Isaac SP, Teo BS, Kang DJ, Tarte EJ, Barber ZH, Evetts JE, Blamire MG, Resistance of a domain wall in $La_{0.7}Ca_{0.3}MnO_3$, *Journal of Applied Physics* **86**, 6287-6290 (1999).

[29] Rzchowski MS and Joynt R, Electronic inhomogeneity at magnetic domain walls in strongly-correlated systems, cond-mat/0304287.

[30] S.A.Kivelson E. Fradkin and V.J.Emery, Electronic liquid-crystal phases of a doped Mott insulator, *Nature* **393**, 550-553 (1998).

[31] K. McElroy et al, Homogenous nodal superconductivity coexisting with inhomogeneous charge order in strongly underdoped Bi-2212, cond-mat/0404005.

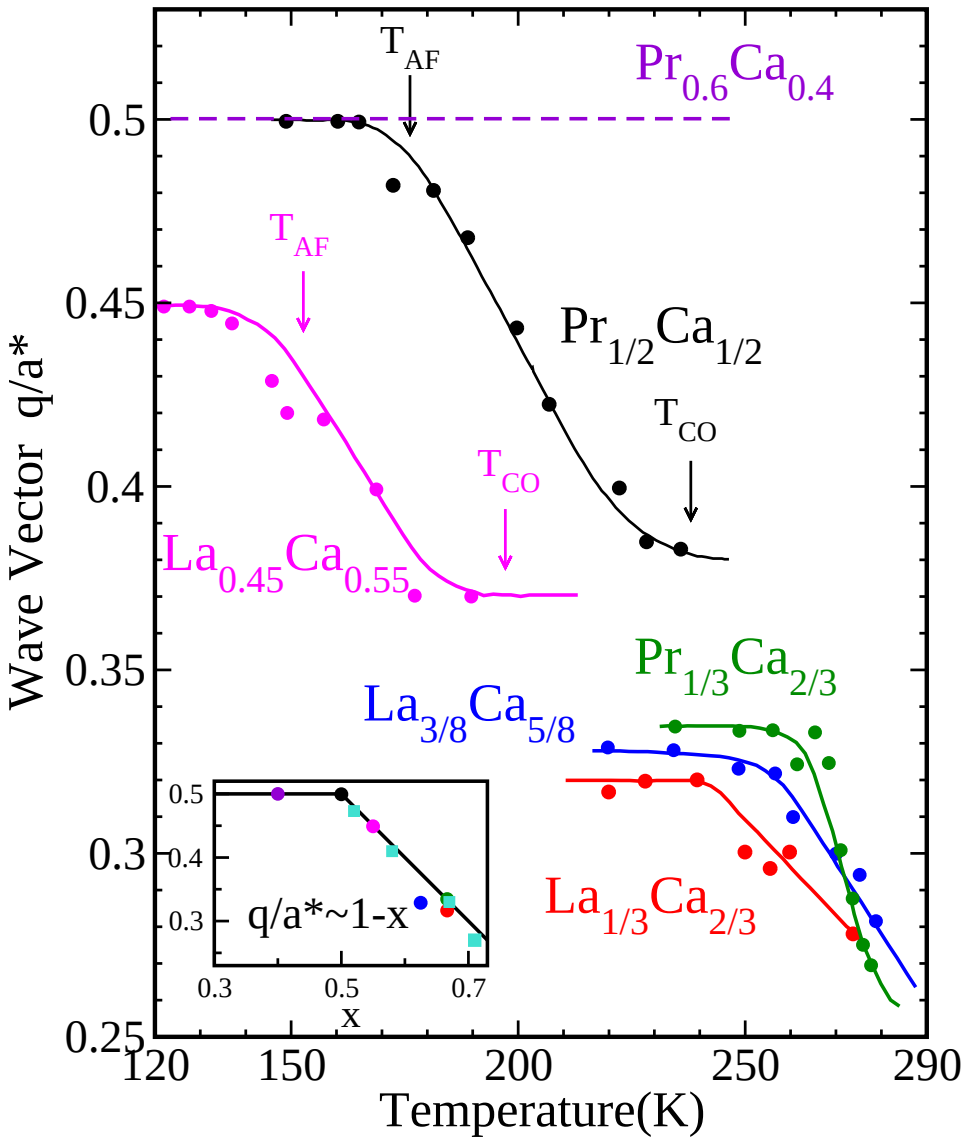

FIG. 1: Wave vector of the modulation $q/a*$ versus temperature for $Pr_{1-x}Ca_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ at different dopings ($x \geq 0.5$ data taken from Figs. 1 and 2 in [20] and $x = 0.4$ taken from [16]). The same kind of behaviour has been reported for $La_{1/2}Ca_{1/2}MnO_3$ [7] (not shown here). At low temperatures $q/a* \approx (1-x)$, as shown in the inset, and decreases above the Néel temperature T_{AF}. The inset shows $q/a*$ versus x as in [17, 19]. The circles correspond to the low temperature values of the curves in the main panel while the squares are data for $La_{1-x}Ca_xMnO_3$ taken from [21].

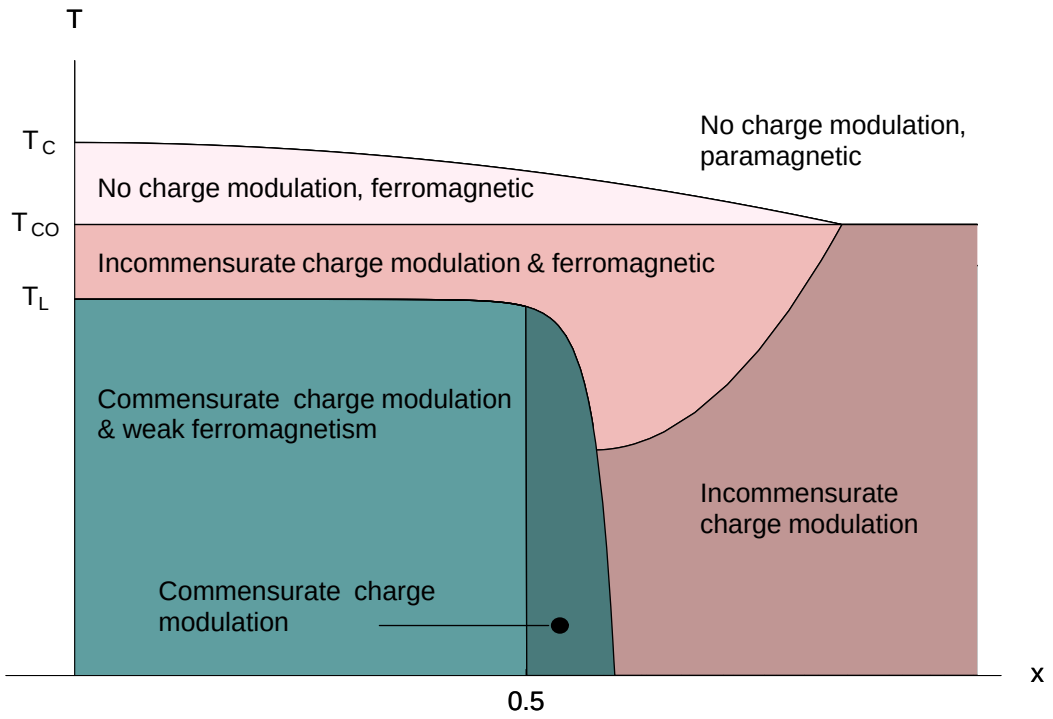

FIG. 2: Schematic phase diagram which results from the minimisation of the free energy. The scale of the axes depends on the particular parameters used. The commensurate order phase just above $x = 0.5$ has not been observed but we predict it can be relevant for dopings very close to $x = 0.5$ for highly insulating manganites. The complex phases arise provided $T_C > T_{CO}$, a condition that can be relaxed if the model is extended to account for discontinuous phase transitions. The values of T_{CO} and T_C are direct parameters in the model whereas the lock-in temperature T_L is a consequence of the competition between the Umklapp and incommensurate modulation terms.

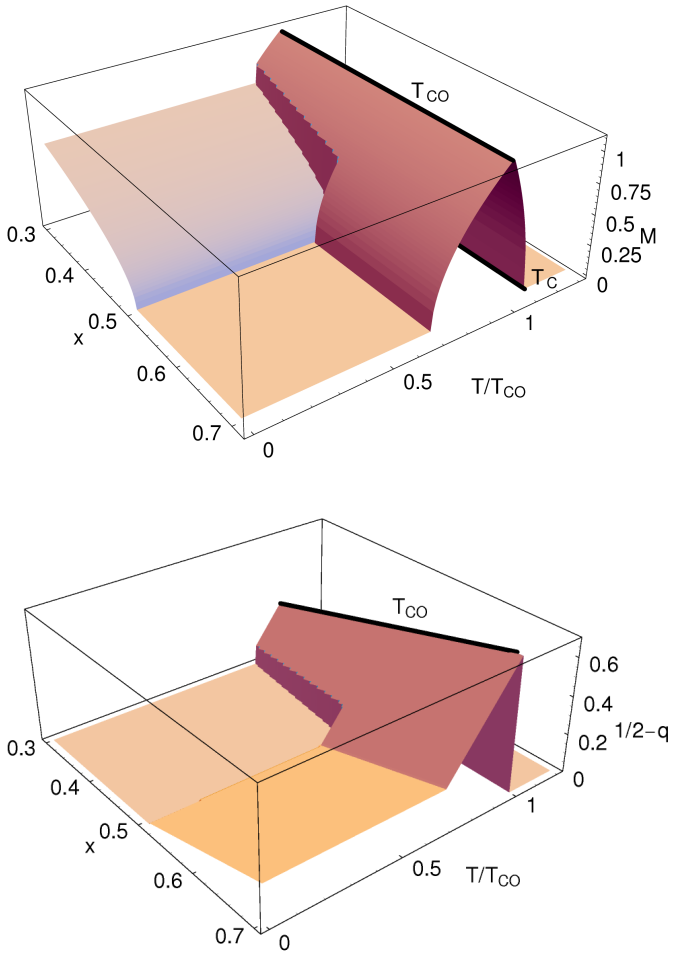

FIG. 3: Results within Phase Modulation Approximation for a particular choice of parameters. These complement and clarify the schematic view in Fig. 2. Top: magnetisation in the doping-temperature plane. The low temperature phases are non magnetic for $x > 0.5$ (corresponding to antiferromagnetism in experiments) and weakly ferromagnetic for $x < 0.5$ (corresponding to the canted antiferromagnetism found in $Pr_{1-x}Ca_xMnO_3$ [18, 24, 25]). Above the Néel temperature there is a reentrant magnetisation that has been reported for $x \geq 0.5$. Bottom: deviation from commensurability $1/2-q$ in the doping-temperature plane. The surface consists of three planes that correspond to commensurate order $\nabla\phi = 0$ for the ground state of the charge ordered underdoped samples, incommensurate order for the overdoped samples that follow $1/2-x$ as shown in the inset of Fig. 1, and a change of wave vector with temperature above the Néel transition as shown in the main panel of Fig.1.

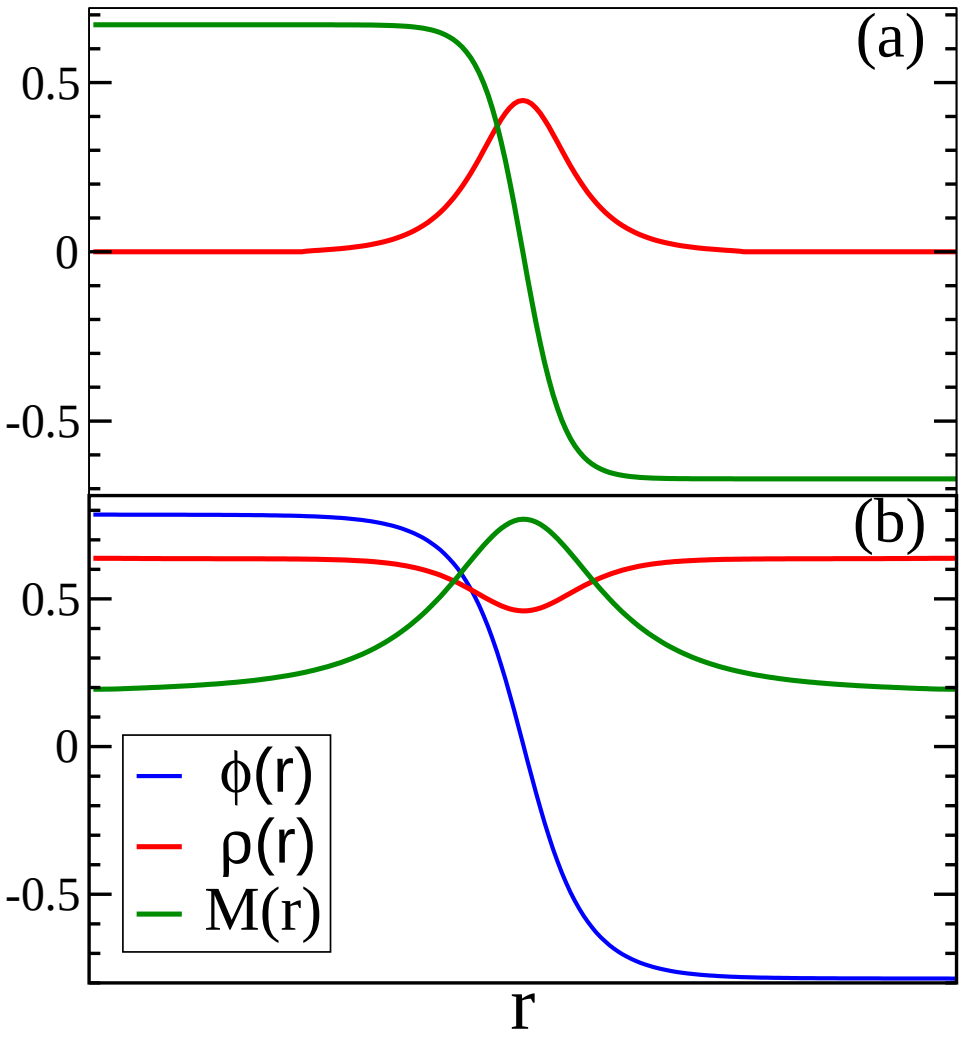

FIG. 4: Example solutions of the total Free Energy when all the order parameters are allowed to change spatially. (a) The magnetisation (green) decays in the centre of a magnetic domain wall leading to the appearance of charge modulation (red). (b) In a discommensuration, the phase of the charge modulation (blue) changes by $\pi/2$, the amplitude of the charge modulation (red) is suppressed, and the magnetisation (green) enhanced.